Sources and Reduction of NOx-Emissions

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Summary:

Cement kiln NOx emissions are between 300 and 2500 mg NO_2 / Nm^3.

The degree of NOx emission is mainly determined by

- Flame temperature
- Oxygen content
- Residence time of exhaust gas in the kiln
- Fuel-N
- Primary measures against NOx
- Secondary measures against NOx

The NOx control technologies available for cement kilns include:

- Combustion Operational Modifications (COM)
- Low NOx Burners (LNB)
- Staged Air Combustion (SAC)
- Selective Non-Catalytic Reduction (SNCR)

1. INTRODUCTION

NOx is produced to different degrees in all stationary and mobile combustion sources. Because of the high flame temperatures the NO generation in cement kilns is relatively high.

2. CHEMICAL AND PHYSICAL PROPERTIES AND ENVIRONMENTAL ASPECTS OF SOME NITROGEN COMPOUNDS AND OZONE

2.1 Nitrogen (N_2)

2.1.1 Physical Properties [1]

At atmospheric pressure and room temperature, nitrogen is a colorless, odorless, non-combustible gas. Nitrogen condenses to a colorless liquid at -195.80°C and 101.3 kPa and forms a white solid at -209.86°C.

M_r	28.0134
Triple point	
T	63.15 K
p	12.463 kPa
heat of fusion	25.8 kJ/kg
Boiling point (101.3 kPa)	77.35 K
heat of vaporization	199 kJ/kg
Critical point	
T_{crit}	126.2 K
p_{crit}	3.39908 Mpa
Q_{crit}	314.03 g/L
Properties at 0°C, 101.3 kPa:	
Relative density (air = 1)	0.967
Specific heat capacity	1.039 $Jg^{-1} K^{-1}$
Dynamic viscosity	15.9×10^{-6} Pa s
Thermal conductivity	23.86 $mWm^{-1} K^{-1}$

2.1.2 Chemical Properties [1]

Nitrogen has an extremely high heat of dissociation:

$$N_2 \leftrightarrow 2\,N \qquad \Delta H_0 = 943.8 \text{ kJ/mol}$$

No marked dissociation takes place even at 3000°C and standard pressure. The strength of the N º N bond is responsible for the inertness of N_2.

Important reactions of nitrogen with non-metals are those with hydrogen, yielding ammonia, and with oxygen. The latter, an endothermic reaction, gives nitrogen monoxide:

$$N_2 + O_2 \leftrightarrow 2\,NO \qquad \Delta H_0 = 180 \text{ kJ/mol}$$

2.2 Nitrogen Oxides (NO, NO_2 N_2O)

2.2.1 Physical Properties [1]

Compounds of oxygen with nitrogen are considered as a class and called nitrogen oxides (often denoted as NOx). The known oxides and their equilibrium reactions are as follows:

			+I	
			N_2O	Dinitrogen monoxide
	+II		+II	
Nitrogen monoxide	NO	↔	N_2O_2	Dinitrogen dioxide
			+III	
			N_2O_3	Dinitrogen trioxide
	+IV		+IV	
Nitrogen dioxide	NO_2	↔	N_2O_4	Dinitrogen tetroxide
			+V	
			N_2O_5	Dinitrogen pentoxide
	+VI		+VI	
Nitrogen trioxide	NO_3	↔	N_2O_6	Dinitrogen hexoxide

Table 1: Physical properties of nitrogen oxides

Compound	**N_2O**	**NO**	**NO_2 / N_2O_4**	**N_2O_3**	**N_2O_5**
Oxidation state	1.000	2.000	+4 / +4	3.000	5.000
T_{cr}, °C	36.410	-93.000	157.850		
p_{cr}, MPa	7.245	6.485	10.132		
Q_{cr}, kg/m^3	452.000	520.000	550.000		
mp, °C	-90.860	-163.650	-11.200	-100.700	32.4*
bp, °C	-88.480	-151.770	21.150	-40 to +3	
Specific heat c_p, kJ kg^{-1} K^{-1}	0.879	0.996	1.326	0.862	0.778
Standard enthalpy of formation $\Delta H°_F$, kJ/kg	1864.190	3007.684	721.199	1101.435	104.589
Heat of vaporization at *bp*, kJ/kg	376.070	459.031	414.257	517.416	
Density, kg/m3 Gas (0°C, 101.3 kPa) Liquid (20°C, 101.3 kPa)	 1.9775 793	 1.3402	 3.4 (20°C) 1446.8	 1.447 (2°C)	 2.05 (solid)
Dynamic viscosity, mPa -s Gas (25°C, 101.3 kPa)	 14.874	 19.184	 12.838		
Thermal conductivity, W m^{-1} K^{-1} Gas (25°C, 101.3 kPa) Liquid (20°C, 101.3 kPa)	0.01718	0.02573	0.1124 0.1336		

* Sublimation point

N_2O

Under normal conditions (i.e. room temperature and atmospheric pressure), dinitrogen monoxide, also called nitrous oxide, N_2O, M_r 44.01, is a colorless gas with a weak, pleasant odor and a sweetish taste. If inhaled, it can bring about a spasmodic inclination to laugh and a condition resembling drunkenness hence, its historic name, laughing gas.

NO

Nitrogen monoxide, also called nitric oxide, NO, M_r 30.01, is a colorless, toxic, nonflammable gas at room temperature. As soon as it comes in contact with atmospheric oxygen, it is oxidized to nitrogen dioxide, a brown vapor.

NO_2

Nitrogen dioxide, NO_2, M_r 46.01, is a brownish red, toxic gas with a pungent odor; for physical properties, see Table 1.

2.2.2 Toxicology [1]

NO

Pure nitrogen monoxide does not have any irritating effects. It reacts, however, with hemoglobin to form methemoglobin, resulting in cyanosis and possible death. The TLV-TWA value is 25 ppm (31 mg/m^3).

NO_2

Nitrogen dioxide is an irritant gas. Its MAK value is 5 ppm (9 mg/m^3). TLV-TWA 3 ppm (5.6 mg/m^3), TLV-STEL 5 ppm (9.4 mg/m^3). Inhalation of nitrogen dioxide causes pulmonary edema which may result in death (lethal dose 200 ppm). The substance is only slightly water-soluble but highly lipid-soluble. It therefore penetrates the alveoli where it damages the capillary walls resulting in exudative inflammation. The respiratory tract is obstructed due to formation of foam.

Concentrations exceeding 60 - 150 ppm produce coughing and a burning sensation in the chest. Pulmonary edema becomes apparent after 2 - 24 h. The patient suffers respiratory distress and insomnia. Chronic exposure to low doses results in coughing, headache, loss of appetite and gastrointestinal disorders. Patients should be kept under clinical observation. Inhalation of ammonia from ammonium hydrogen carbonate is recommended.

N_2O

Dinitrogen monoxide (laughing gas) does not irritate the mucous membranes. It has a powerful analgesic action but is only weakly narcotic. The gas displaces nitrogen from air-filled body cavities (middle ear, sinuses, intestines, brain ventricles) resulting in an increase in pressure. After chronic exposure, polyneuropathy and myelopathy have been observed. TLV-TWA value is 50 ppm (90 mg/m^3).

2.2.3 Environmental Aspects [2]

Conditions which produce nitrogen oxides do not occur solely in stationary combustion sources. The exhaust gases from **internal-combustion engines**, particularly those of the gasoline-burning spark-ignition variety, contain traces of nitrogen oxides, and because of the sheer number of them they are estimated to contribute about 50% of the total anthropogenic NOx burden.

Vehicle exhaust also contains the other ingredients needed to produce the effect known as photo-chemical smog; this has long plagued large conurbations in badly ventilated situations such as Los Angeles, Tokyo and Mexico City, and it has more recently become a feature of many other urban centers. The nitrogen oxides, activated by solar ultraviolet, react in the urban atmosphere with the unburned hydrocarbons from vehicle exhausts to produce a noxious cocktail of corrosive, oxidizing and irritating chemicals such as organic peroxides.

They also interact with atmospheric oxygen to produce ozone. It is ironic that, at a time when one form of atmospheric pollution is destroying the ozone in the stratosphere, which provides vital protection against excessive solar radiation at the surface, another is creating it near ground level, where it is an economic and health hazard. Vehicle exhaust is, of course, discharged virtually at ground level, and its effects are "local" rather than global: the smog pall from Los Angeles sometimes extends 100 miles or more inland.

But nitrogen oxides are now known to be a key component of a much more widespread problem which is even more serious in terms of its international implications than is photochemical smog. It is now plain that a sizable proportion of the blame for the very topical environmental concern of acid rain which was formerly perceived as an effect only of sulfur oxides, can in fact be attached to nitrogen oxides. Acid rain which ought really to be termed "acid precipitation" since the most spectacular manifestations tend to occur in snow rather than rain is no observer of national boundaries. Pollutants released in one country may come to earth in precipitation not just in neighboring countries but even in other continents.

As the extent of the problem and its causes have become better understood and documented, it has become the subject of international dispute and negotiation. Ecological damage to the forests and lakes of Eastern Canada has been ascribed to (amongst other things) acidity originating from industrial sources in the US Mid-West. Similar damage which has ravaged the forests and lakes of Scandinavia has been blamed on pollution exported from the nearer EEC countries, especially the United Kingdom and Germany, and former communist central European countries such as Poland, Czechoslovakia and Romania. And since the communist regimes in these countries collapsed the appalling extent of the devastation of their own forests has become only too apparent.

By what mechanism acid rain causes forest damage is not known for certain. Two theories are currently given greatest credence. One proposes that the acidity leaches cationic nutrients such as calcium, magnesium and potassium away from the root zone and down into the subsoil, causing starvation. The other postulates that the acidity solubilizes normally immobile aluminum in the soil; this interferes with the normal uptake of other cationic nutrients and, if it reaches a threshold concentration (which varies according to the species of tree), it is directly toxic. This could also explain the dire effect on the aquatic life of lakes and rivers in the affected regions.

Other pollutants reckoned to damage forests include heavy metals which are given off in coal smoke as well as in emissions from metal smelters and ozone which - as already mentioned - is generated in interactions between waste nitrogen oxides and atmospheric oxygen.

Studies made in the United States for the National Acid Precipitation Assessment Program (NAPAP) - a statutory body set up under the acid Precipitation Act of 1980 - have shown that the acidity is worse in high-level rain clouds than in lower-level clouds, suggesting that the pollutants causing it are carried up into the higher levels rather than diffusing up from ground level. So, while it is necessary to tackle exhaust emissions from vehicles to alleviate the smog problem and any strategy for curbing **the contribution of nitrogen oxides to acid rain must center on the control of emissions from the large stationary sources.**

2.3 Ammonia

Ammonia, NH_3, occurs in nature almost exclusively in the form of ammonium salts. Natural formation of ammonia is primarily by decomposition of nitrogen-containing organic materials or through volcanic activity. Ammonia and its oxidation products which combine to form ammonium nitrate and nitrite, are produced from nitrogen and water vapor through electrical discharges in the atmosphere.

These ammonium salts, as well as those arising from industrial and automotive exhausts, supply significant quantities of the nitrogen needed by growing plants when eventually deposited on the earth's surface. Ammonia and its salts are also byproducts of commercial processing (gasification, cooking) of fuels with vegetable origins such as coal, lignite and peat.

2.3.1 Physical Properties

M_r	17.0312
Liquid density (at -33.43°C, 101.3 kPa)	0.682 g/cm^3
Gas density (at -33.43°C, 101.3 kPa)	0.888 g/L
Melting point (triple point)	-77.71°C
Vapor pressure (triple point)	6.077 kPa
Boiling point (at 101.3 kPa)	-33.43°C
Heat of vaporization (at 101.3 kPa)	1370 kJ/kg
Standard enthalpy of formation (gas at 25°C)	-45.72 kJ/mol
Net heating value, LHV	18.577 kJ/g
Gross heating value, HHV	22.543 kJ/g
Ignition temperature acc. to DIN 51 794	651°C
Explosive limits	
NH_3 - O_2 mixture (at 20°C, 101.3 kPa)	15 - 79 vol % NH_3
NH_3 - air mixture	
(at 0°C, 101.3 kPa)	16 - 27 vol% NH_3
(at 100°C, 101.3 kPa)	15.5 - 28 vol% NH_3

2.3.2 Chemical Properties

Gaseous ammonia reacts very violently to explosively with nitrogen oxides to form nitrogen, water, ammonium nitrate or nitrite. The reaction with N_2O does require ignition.

2.3.3 Toxicology

Ammonia is a strong local irritant. On mucous membranes alkaline ammonium hydroxide forms which dissolves cellular proteins and causes severe necrosis (corrosive effect).

Ammonia or ammonium hydroxide can penetrate the cornea rapidly, leading to keratitis, damage of the iris, cataract and glaucom.

Oral ingestion of aqueous ammonia can corrode the mucous membranes of the oral cavity, pharynx and esophagus and cause the shock syndrome, toxic hepatitis and nephritis.

Ammonia is absorbed rapidly by the wet membranes of body surfaces as ammonium hydroxide, converted to urea and excreted by the kidneys.

Human Exposure: Concentrations of 50 ppm are perceived easily; 50 - 72 ppm does not disturb respiration significantly. Levels of 100 ppm irritate nose and throat and cause a burning sensation in the eyes and tachypnoe. In addition to the symptoms described above, 200 ppm induce headache and nausea; 250 - 500 ppm, tachypnoe and tachycardia; 700 ppm, immediate onset of burning sensations in the eyes; 1000 ppm causes immediate coughing.

The nitrogen metabolism is not significantly changed after exposure to 500 ppm of ammonia.

The TLV value has been set at 25 ppm with a short-term limit exposure value at 35 ppm; the MAK is established at 50 ppm.

2.4 Ozone

Ozone is thermodynamically unstable and spontaneously reverts back into diatomic oxygen. This process is promoted by the presence of transition metals or their oxides.

An irritating pale blue gas, ozone is explosive and toxic, even at very low concentrations. At -111.9°C it condenses to form a dark violet liquid which freezes at -192.7°C. In the Earth's stratosphere, it occurs naturally (5-10 ppm), protecting the planet and its inhabitants by absorbing ultraviolet radiation of wavelength 290-320 nm.

2.4.1 Physical Properties

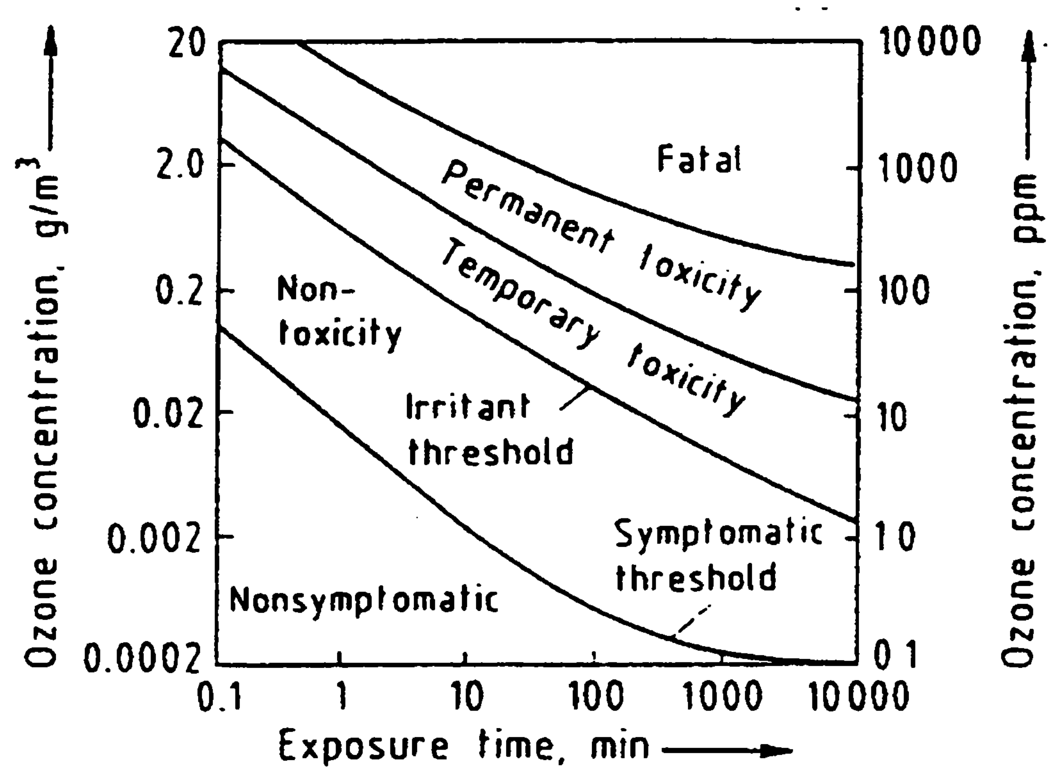
M_r	48.0
bp (101 kPa)	-111.9°C
mp	-192.7°C
Critical temperature	-12.1°C
Critical pressure	5.53 MPa
Critical density	437 kg/m^3
Critical volume	1.471 x 10-4 m^3/mol
Heat capacity, gas	
0°C	794 $Jkg^{-1} K^{-1}$
25°C	818 $Jkg^{-1} K^{-1}$
Heat of vaporization	15.2 kJ/mol
Heat of formation	144.8 kJ/mol

2.4.2 Toxicity

Ozone, being an extremely powerful oxidizing agent, readily oxidizes a variety of functional groups in biochemicals. Studies indicate that free radical formation, lipid peroxidation, carbonyl and aldehyde formation, and oxidation of SH groups, are some of the major sites of attack. Ozone readily reacts with olefinic compounds, particularly polyunsaturated lipids, forming unstable ozonides. Their decomposition results in the formation of toxic free radicals which can in turn amplify the primary cytotoxic or tissue damage. While ozone is considered to be a toxic gas, there are factors which mitigate the immediate danger to individuals working with it. Toxicity is dependent on concentration and length of exposure. OSHA has set an 8-h TWA-PEL of 0.2 mg/m³ (0.1 ppm) for ozone.

Fig. 1 illustrates the relationship between various exposure levels and exposure time for humans. The odor threshold concentration for ozone is approx. 0.02-0.04 mg/m³ (0.01 - 0.02 ppm).

Figure 1: Human toxicity limits for ozone exposure



2.4.3 Formation of Trophospheric Ozone

$$CO + OH \rightarrow H + CO_2$$

$$H + O_2 H M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$NO_2 + \text{Light } (\lambda < 420 \text{ nm}) \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

Net: $CO + 2\,O_2 + \text{Light } (\lambda < 420 \text{ nm}) \rightarrow CO_2 + O_3$

3. PRESENT SITUATION

3.1 Present State of Cement Kiln Emission

There is no normal or average NO_x emission from cement kilns. Many factors like kiln system and fuel characteristics are influencing the NO_x emission.

3.2 Present Legal Situation [16]

All combustion processes primarily produce nitrogen monoxide NO with a much smaller proportion of nitrogen dioxide NO2 (of the order of 5%). In the free atmosphere, i.e. at relatively low temperature, however, nitrogen monoxide is oxidized further to form nitrogen dioxide NO2. Owing to this oxidation, no difference is made between the two gases when emissions are concerned and they are referred to generally under the formula NO_x (= NO + NO2 expressed as NO2), or nitrogen oxides. However, decisive for the NO_x emission is the formation of nitrogen monoxide (NO) in the kiln system.

Emission Limits

Nm^3_{dry} = m^3 at 273 K, 101300 Pa and 0% water

Europe	200 - 1800 mg / Nm^3
Germany	
new plants / modification	500 mg / Nm^3_{dry}
existing plants	800 mg / Nm^3_{dry}
100% waste burning (17. BImSchV)	200mg / Nm^3_{dry}
USA	720 - 1100 mg/Nm^3

US plants burning hazardous waste are regulated under BIF (Burners and Industrial Furnaces). Other plants do have a state permit defining certain parameters like NO_x, SO_2, CO and THC emission. The limits for these emissions are called emission standards. This standards are individually defined for each plant and usually represent the operating situation under certain conditions. Therefore, the US standards are different from the emission limits in Europe where emission limits are valid for a whole state or country.

For comparison reason all emission limits/standards are indicated in mg/Nm^3. The emission standards in the USA are usually not using mg/Nm^3 but ppm, $lb/t_{dry\ feed}$, gr/dscf, $lb/1000lb_{gas}$, lb/hr, etc. To convert them into mg/Nm^3 certain assumptions were necessary.

All the above explained emission limits do include definitions how and when the compliance tests have to be carried out. It is, e.g. a very important difference whether the emission has to be measured continuously or not.

4. NITROGEN INPUT INTO THE KILN SYSTEM

Nitrogen is introduced into the kiln system as molecular nitrogen (N_2) in the combustion air (primary, secondary, tertiary) and as nitrogen compounds in the fuel. The quantity of the relevant N_2 introduced into the kiln system is defined by the stoichiometric air required for the combustion plus excess air.

The concentration of N_2 in the air is always 78%.

The quantity of fuel-N is defined by the fuel input and the nitrogen content in the fuel:

Heavy oil:	700 - 1000 ppm by mass of N
Coal:	1000 - 4000 ppm by mass of N

5. BEHAVIOR OF NITROGEN IN THE PROCESS

5.1 NO Formation

NO formation only occurs at elevated temperatures (> 800°C). It is always connected with the combustion process.

5.1.1 Nitrogen Monoxide Formation Reaction Mechanism

The formation of nitrogen monoxide is not a simple process that can be described by a few equations. The complexity of the reactions involved has hitherto prevented the formulation of a conclusive theory regarding the formation of nitrogen monoxide NO. However, it appears to consist essentially of two phenomena, the products of which are referred to as "thermal NO" and "fuel NO".

"Thermal NO"

The "thermal NO" is produced by the oxidation of molecular nitrogen in the combustion air according to the formula:

$$N_2 + O_2 \rightarrow 2\,NO \quad (0)$$

"Fuel NO"

The "fuel NO" is produced by the oxidation of organically bonded nitrogen in the fuel.

Formation of "Thermal NO"

In the zone of combustion products that is after the flame front (oxidation zone), "thermal NO" is produced if the combustion gases remain for a sufficiently long time at temperatures above about 1600°C. This is determined by what is known as the Zeldovich mechanism according to the reactions:

$$N_2 + O^{\bullet} \rightarrow NO + N^{\bullet}\ (K1)\ ;\ N_2 + O^{\bullet} \leftarrow NO + N^{\bullet}\ (K2) \qquad (1, 2)$$

$$N^{\bullet} + O_2 \rightarrow NO + N^{\bullet}\ (K3)\ ;\ N^{\bullet} + O_2 \leftarrow NO + O^{\bullet}\ (K4) \qquad (1, 2)$$

Here the speed is governed by that of the fastest reaction, i.e. the reaction between atomic oxygen (radical) and the nitrogen molecule. The rate of formation is therefore proportional to the concentration of atomic oxygen and molecular nitrogen. Assuming that combustion takes place in the presence of an air surplus, the following equation is obtained:

$$\frac{d[NO]}{dt} \sim 2 \bullet K_1 \bullet [N_2] \bullet [O^\bullet] \qquad (4)$$

The pronounced dependence of K_1 on temperature can be seen in Fig. 3. Thus, at high temperatures the equilibrium of the reaction is on the side of NO formation.

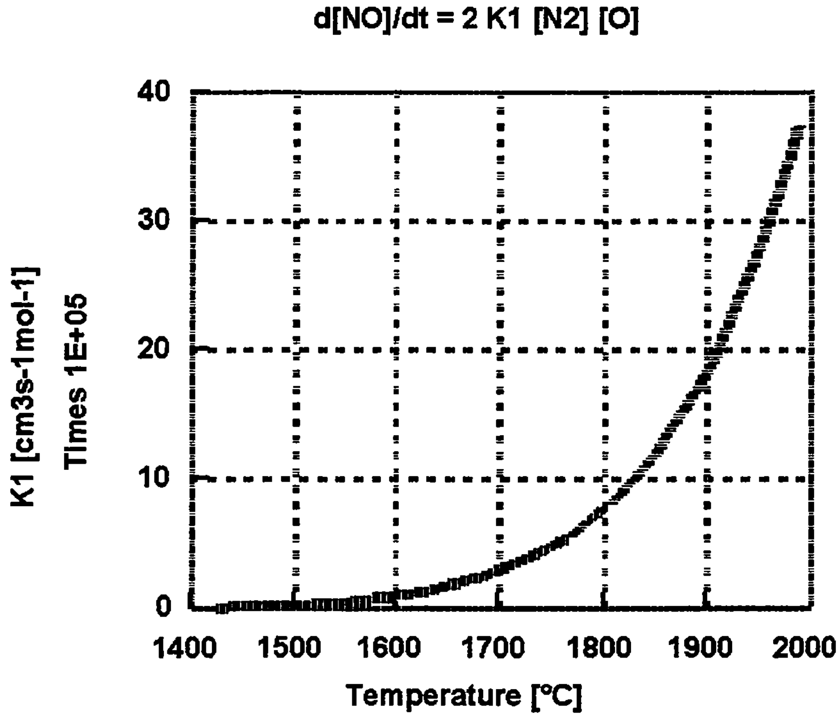
In the flames of rotary cement kilns the atomic oxygen primarily comes from the thermal dissociation of O_2:

$$O_2 \leftrightarrow 2\,O^\bullet \qquad (5)$$

Therefore, for the formation of NO the following equation is obtained:

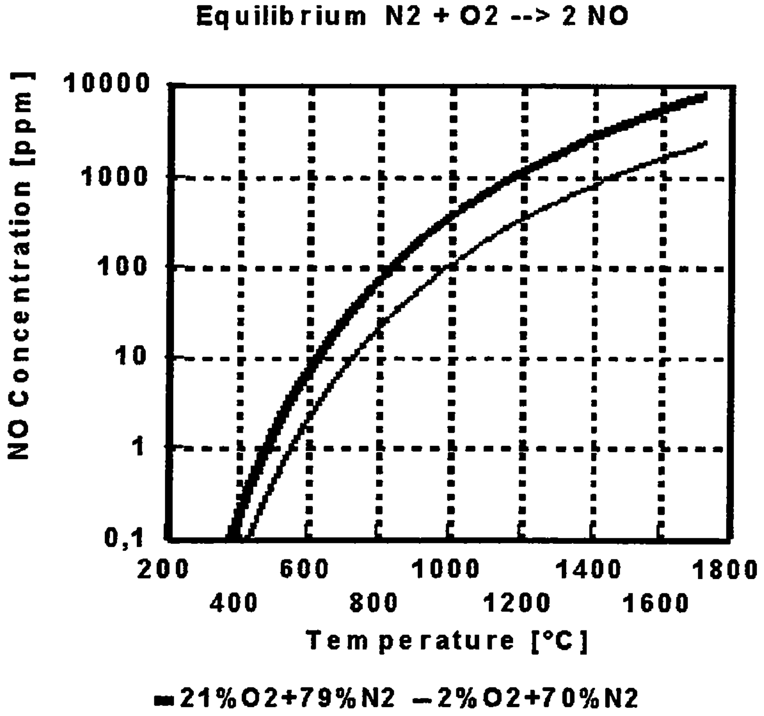
$$\frac{d[NO]}{dt} = K \bullet [N_2] \bullet [O^\bullet]^{1/2} \qquad (6)$$

Figure 3: **Dependence of K_1 on temperature**



The amount of nitrogen monoxide actually produced during technical combustion processes is a long way below equilibrium concentration (cf Fig. 4) owing to the marked dependence on temperature of the NO reaction and the relatively short time that it remains at this temperature. In air 50% of the equilibrium value is attained at temperatures around 2000°C but only after about 2.5 seconds. The dwell time of the gas in the flames of rotary cement kilns are obviously a whole order of magnitude below that. Thus, if the gases remain for a long time at high temperatures, the formation of NO is favored.

Figure 4: **Equilibrium $N_2 + O_2 \rightarrow 2\ NO$**



Hence, the formation of "thermal NO" is governed by the following parameters:

- Temperature
- Gas composition
- Dwell time at high temperature

Formation of "Fuel NO"

Fossil fuels contain varying proportions of nitrogen compounds:

Heavy oil:	700 - 1'000 ppm by volume of N
Coal:	1'000 - 4'000 ppm by volume of N

Already during the pyrolysis of these fuels, i.e. at relatively low temperatures, the nitrogen compounds break off as secondary compounds, such as amines and cyanides, which are then oxidized by OH radicals or O_2 to form nitrogen monoxide, or which react with nitrogen compounds (mainly NO) to form molecular nitrogen. The formation of NO from fuel nitrogen occurs almost regardless of how it is bonded, but is largely influenced by the amount of nitrogen contained in the fuel. It can be assumed that all fuel-bonded nitrogen compounds finally adopt a composition "I", where "I" may be either NH_2 or atomic N. These are then converted into either NO or N_2:

$$I + OX \rightarrow \ldots \rightarrow NO + \ldots \qquad (7)$$

$$I + NO \rightarrow \ldots \rightarrow N_2 + \ldots \qquad (8)$$

Hence, the formation of "fuel NO" is governed by the following parameters:

- The formation of NO depends on the quantity but not of the nature of nitrogen compounds contained by the fuel
- With increasing air surplus the proportion of nitrogen compounds in the fuel converted into NO increases
- Under sub-stoichiometric conditions it is possible for NO to be converted into N_2. This takes place by combination of the NO with atomic nitrogen present in large proportions in the flame according to the formula:

$$NO + N^{\bullet} \rightarrow N_2 + O^{\bullet} \qquad (9)$$

- The conversion of nitrogen compounds in the fuel to NO depends to a large extent on the design of the burner of the precalciner. Here such operations as
    - heating and distribution of drops or particles in the combustion air
    - driving off the volatile part
    - heterogeneous combustion
    - etc.

play a very important role

5.1.2 NO-Decomposition Mechanism in the Combustion Process

Homogeneous Reaction

NO reacts with hydrocarbon radicals according to equation 10. The product HCN reacts later like fuel-N and can form NO as well as N_2.

$$CH_x \bullet + NO \xrightarrow{k_{10}} HCN + OH_{(x-1)} \qquad (10)$$

For a significant NO-decomposition according to (10) high hydrocarbon concentration and low air factor (~0.6 - 0.9) are required.

Also reactions between NO and HCN as well as ammonia from the fuel do have an influence on NO-decomposition.

Heterogeneous Reaction

NO can also be reduced on catalytic active surfaces of solids outside of the flame. As catalyst can act coal and ash particles and metal oxides. Prerequisite for this reaction is the presence of CO or H_2 in the exhaust gas. In case of coal particles also a gas-solid reaction between NO and the coal can decompose NO.

The gas-gas reaction proceeds according to equations 11 and 12.

$$NO + CO \xrightarrow{k_{11}} 0.5\, N_2 + CO2_2 \qquad (11)$$

$$NO + H_2 \xrightarrow{k_{12}} 0.5\, N_2 + H_2O \qquad (12)$$

5.2 Formation of Nitrogen Monoxide in a Cement Kiln

If the formation of nitrogen monoxide (NO) in a kiln has to be considered, it has to be distinguished between the formation of NO in the main firing system of the rotating part and its formation in a secondary firing system, if present.

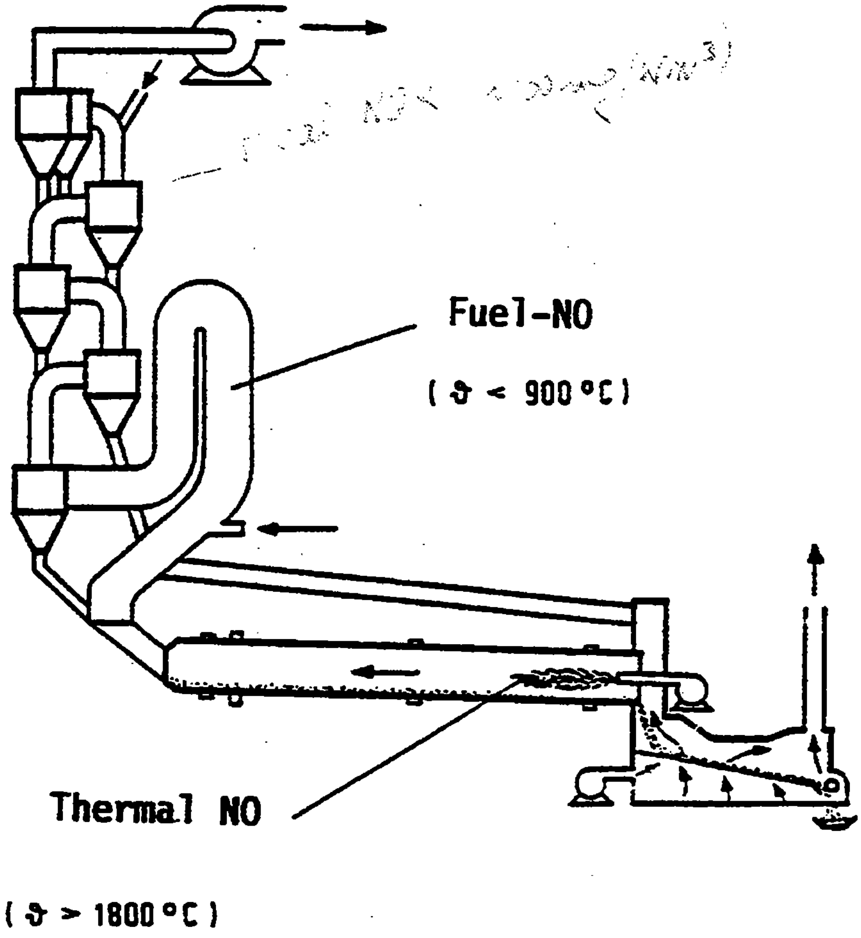
NO Formation in the Main Firing System (rotary part)

In the firing system of a rotary kiln turbulent diffusion flames are used in which the greater part of the combustion air is only fed in after the fuel has been ignited (secondary air, proportion about 90%). As a result a severely sub-stoichiometric pyrolysis zone and flame front are produced. The nitrogen compounds in the fuel are therefore converted into NO to only a small extent. This means that only few "fuel NO" is produced, the nitrogen in the fuel is converted into N_2. In the zone of the combustion products (flue gas) temperatures up to 1800°C are attained and there "thermal NO" is produced. Thus, in the flames of the main firing systems it is mainly "thermal NO" that is produced.

NO Formation in Secondary Firing Systems

In a secondary firing system the fuel fed in burns at much lower temperatures (800 to about 1200°C) than in the main firing system. This means that the NO produced in the secondary firing system cannot have formed thermally, i.e. from N_2 and O_2 of the combustion air. In other words, it is primarily "fuel NO" that is produced in a secondary firing system.

Figure 5: **Regions where NO formation occurs in a rotary kiln plant with cyclone preheater, calciner and tertiary air duct**



Kilns without secondary firing

All kilns without secondary firing, i.e. wet process kilns, long dry process kilns and preheater kilns without riser duct firing, have one thing in common, viz. NO emission is determined exclusively by the conditions in the kiln burning zone. After leaving the burning zone, the kiln gases drop rapidly in temperature to a level at which the NO in the gas decomposes very slowly.

Wet kilns are characterized by a specific heat consumption which is 1.5 to 2 times the specific heat consumption of a preheater kiln. This means a high specific amount of exhaust gas. On the other hand, the high specific combustion air consumption will also mean a somewhat lower secondary air temperature. This combined with the long material retention time in the burning zone should reduce the NOx concentration in the exhaust gas from the burning zone.

SP kiln systems with riser duct firing

In many SP kiln systems 10 - 20% of the fuel is fired into the riser duct. Measurements at several riser duct fired kiln systems indicate that firing coarse fuel (e.g. old tires) into the kiln riser duct will reduce NOx emission from the kiln system.

This is probably explained by the fact that a large part of the fuel directly falls down into the kiln charge, creating a reducing atmosphere in the bottom part of the kiln back-end in which NOx from the burning zone is reduced.

Conversely, when firing finely ground fuel into the kiln riser duct, the specific NOx content in the exhaust gas will often increase on passing through the riser duct.

As the NOx emission from the kiln may also increase slightly due to an increased excess air rate the total NOx emission from the kiln system will often increase when starting up riser duct firing with finely ground fuel.

Precalcining kiln systems

In precalcining kiln systems with tertiary air duct, firing into the rotary kiln typically accounts for only 40 - 50% of the total heat consumption and the specific amount of combustion gases from the kiln burning zone is reduced proportionally. On the other hand, the NOx concentration in the kiln gas may be considerably higher than in preheater kilns.

This is probably due to the shorter material and longer gas retention times in the precalciner kiln burning zone combined with a very high secondary air temperature.

When examining the contribution from the calciner firing to the emission of NOx, we must distinguish between two basically different types of precalcining kiln systems, viz. the In-Line (ILC) type in which the kiln gas passes the firing region of the precalciner and the Separate Line (SLC) type in which the kiln exhaust gas bypasses the firing region of the precalciner.

ILC systems

In these systems the fuel combustion in the calciner takes place in a mixture of kiln exhaust gas and hot air from the cooler (tertiary air). Some of the nitrogen in the fuel reacts with NO from the kiln exhaust gas while another part reacts with oxygen (from the tertiary air) to form NO.

The result may be a net production as well as a net reduction of NO in the calciner. However, in most cases the calciner contributes a little to the NO emission.

SLC systems

In these systems the combustion in the calciner takes place in pure hot air. In the case of oil firing, NO production in the calciner is negligible, but when applying fuels containing nitrogen up to 50% of the nitrogen compounds in the fuel may be converted into NO. The specific NO production in the SLC calciner may be as high as 4 lb NO2/st (1400 mg NO_2/Nm3). This was measured in a calciner fired with pet coke which has a high content of nitrogen and a low content of volatiles.

The NO in the calciner exhaust gas is added to the NO in the gas from the rotary kiln which leaves this type of kiln system without being reduced. When fired with solid fuels, SLC systems must therefore be expected to generate somewhat higher NOx emissions than ILC systems.

5.3 Main Influencing Variables for NO Formation

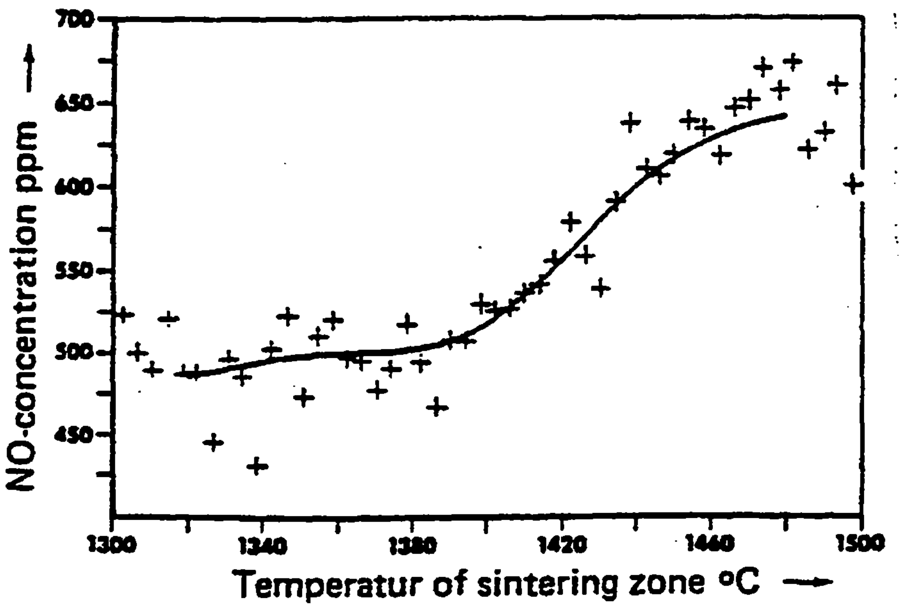
Table 2: NOx forming mechanisms in the kiln system

NO Formation	Main influencing variables	
thermal NO	◆ temperature	• flame shape • temperature peaks in flame • secondary air temperature • burning zone temperature
	◆ oxygen concentration	• flame shape • ignition point • burner momentum • excess air • recirculation • reducing zone • primary air component • swirl intensity
	◆ residence time	• flame shape • kiln diameter
fuel NO	◆ fuel nitrogen content	•
	◆ oxygen concentration ◆ volatiles concentration in the fuel	• flame shape • excess air • recirculation • reducing zone • primary air • swirl intensity
	◆ residence time	• flame shape • gas speed

5.3.1 Temperatures

In Chapter 3.1 it is shown that the NO forming reaction is accelerated exponentially with the temperature. The temperature of the combustion gas is defined by heat generated in the flame and the heat radiation from the burning zone. Temperature has a major influence on NO formation.

Figure 8: Influence of the sintering zone temperature on the NO concentration in the waste gas



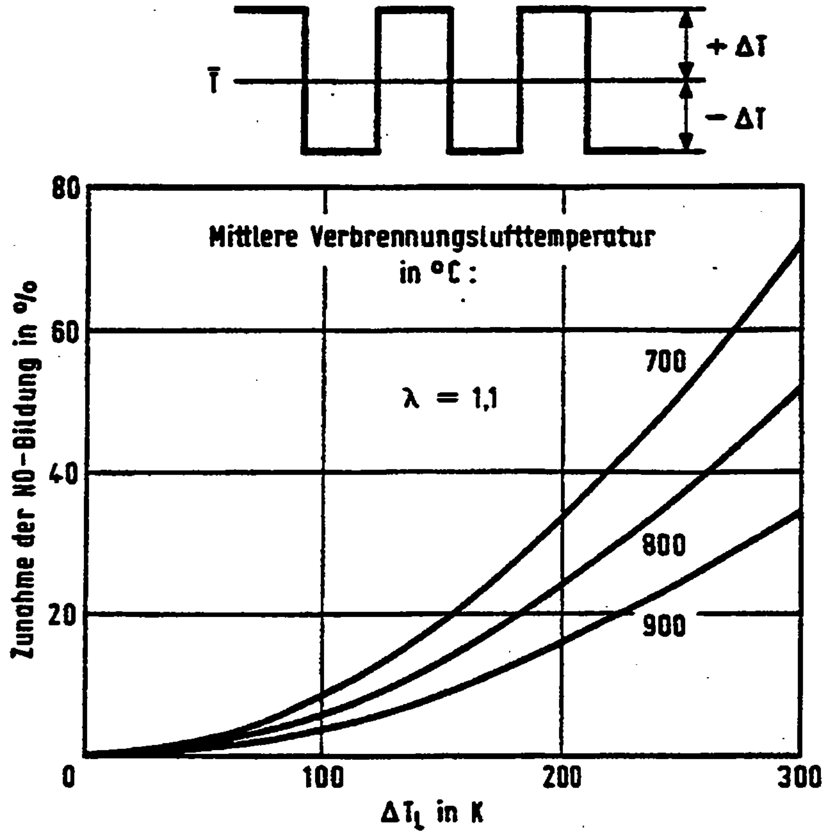
5.3.2 Temperature Peaks [6]

Fig. 9 shows the increase in thermal NO formation due to temperature peaks in an ideal chemical reactor for different amplitudes of a given temperature behavior. For calculating the curves, first the NO concentrations for the temperatures $\overline{T} + \Delta\overline{T}$ and $\overline{T} - \Delta T$ were calculated, averaged and then referred to the NO concentration for $\overline{T}$.

The subscript "L" in the diagram characterizes the combustion air temperature before the start of combustion. It appears from the diagram that the increase in NO formation becomes greater with increasing amplitude DT and decreasing average combustion air temperature. For practical purposes it is important that NO formation can increase by as much as 20 - 40 % even for very small amplitudes of the gas temperature, e.g. 100 K.

Temperature peaks arise more particularly if, in a given combustion chamber, the momentum and angle of exit of the swirl air and axial air of the rotary kiln burner cannot be optimally adjusted to each other or if short-term fluctuations in the fuel feed occur. Modern burners should therefore offer the greatest possible scope for varying their settings.

Figure 9: **Calculated increase in NO formation based on local or time-dependent temperature differences with the average combustion air temperature as parameter**



5.3.3 <u>Excess Air</u>

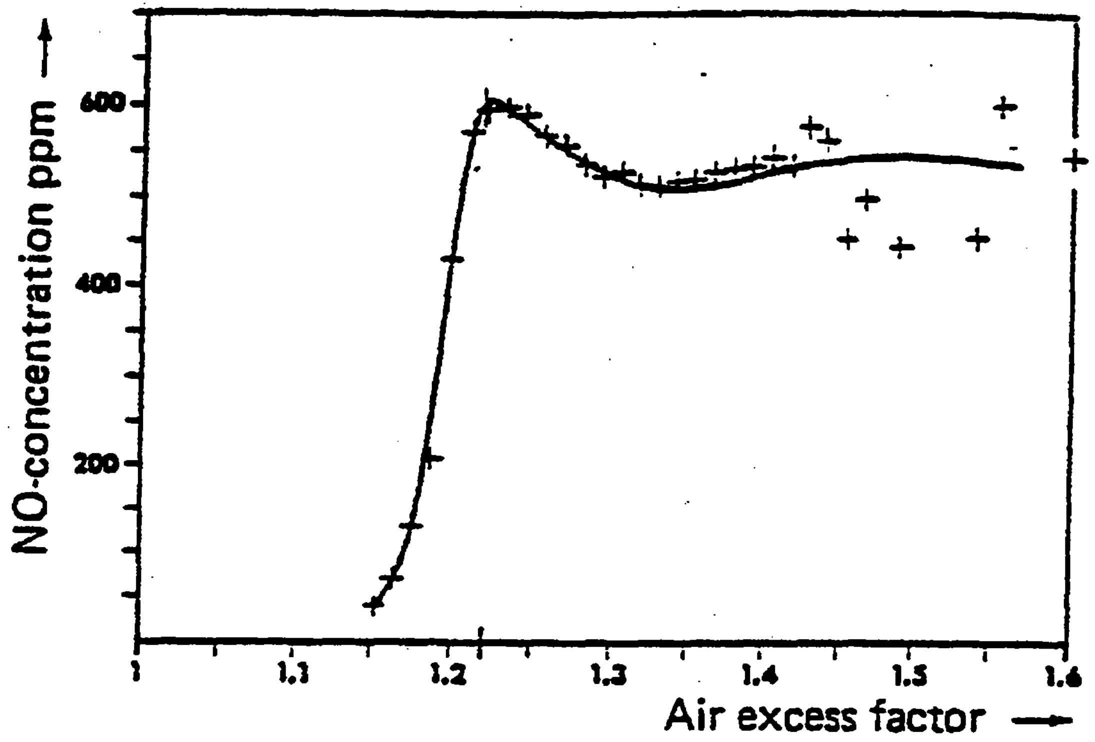
Fig. 10 shows the behavior of NO concentration in the waste gas. The graph can be subdivided into two areas:

A) Air excess factor < 1.2. The NO concentration increases exponentially with the O_2 concentration. This is according to the explanation in chapter 5.1 NO formation.

B) Air excess factor > 1.2. The NO concentration is not anymore a function of O_2. The high amount of excess air is cooling the flame, reducing the residence time of the gas in the kiln and diluting the exhaust gas. These 3 factors are reducing NO generation and concentration in the exhaust gas.

For most kiln systems the excess air factor is below 1.2. Therefore, oxygen concentration has a major influence on NO formation.

Figure 10: Influence of excess air on the NO concentration in the waste gas



5.3.4 <u>Retention Time</u>

The longer the combustion gas remains in the very hot part of the kiln (burning zone), the higher is the NO formation yield.

5.3.5 <u>Burner Operating Parameters</u>

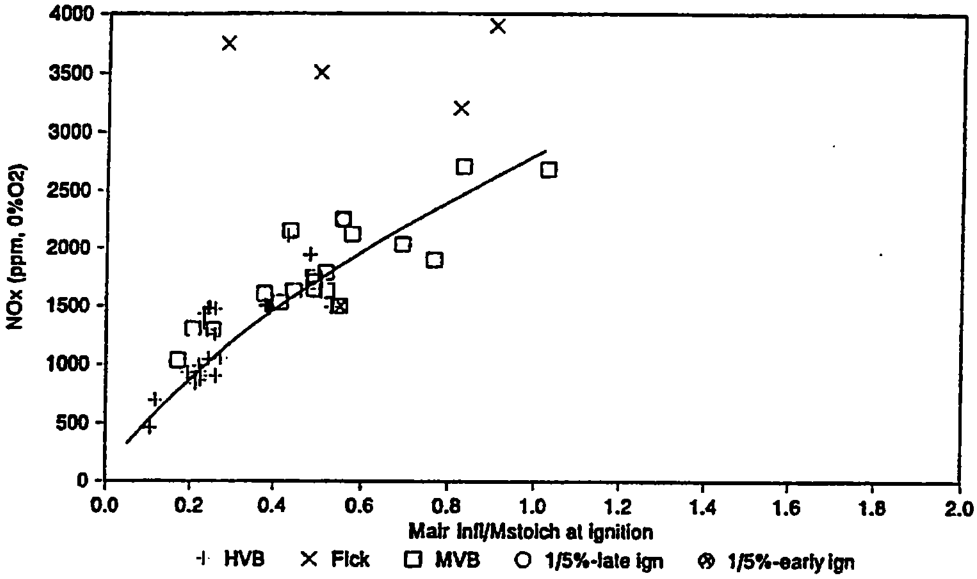
The following burner operating parameters are influencing the flame characteristics (see [13]).

For specific information about formulas and definitions of burner aerodynamics see chapter 6 report PT 96/14078/E.

5.3.5.1 In-flame Air Level at Ignition

A minimum of air shall be entrained into the flame prior to ignition. This can be achieved by a low primary air input and the optimum use of an internal recirculation zone generated by a bluff body and/or swirl.

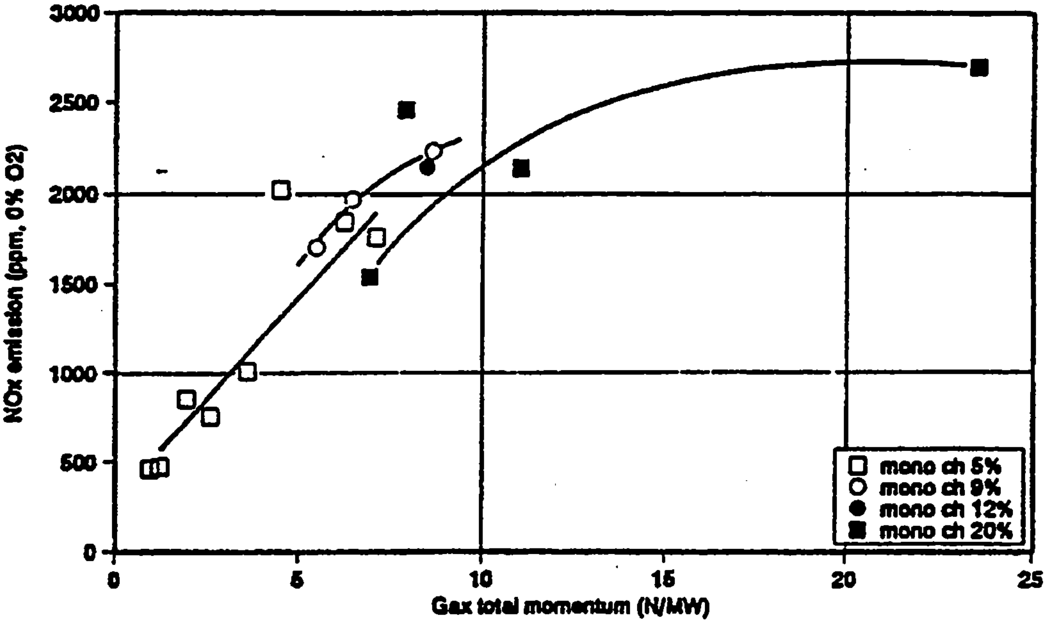
Figure 11:



5.3.5.2 Total Axial Momentum

Total axial momentum affects the overall entrainment into the flame jet. In general higher axial momentum result in enhanced mixing and higher NOx emission levels. For mono channel firing the axial momentum can be observed as a single parameter but for multi channel types a change in axial momentum also influences the tangential momentum.

Figure 12: Influence of Total Axial Momentum on NOx for Mono Channel Burners



From the Cemflame I research study it was finally concluded, that the total axial momentum should be in the range of 3 up to max. 7 N/MW.

This matter of fact however can be confirmed by the old rule of thumb, which states that the kinetic energy of the primary air jet should be kept constant within certain limits.

Applied for a typical kiln system, this formula illustrates as follows:

Figure 13: **Basic Data: Production 3000t/d, Heat consumption 3140kJ/kgc, CV Coal 27.2MJ/kg**

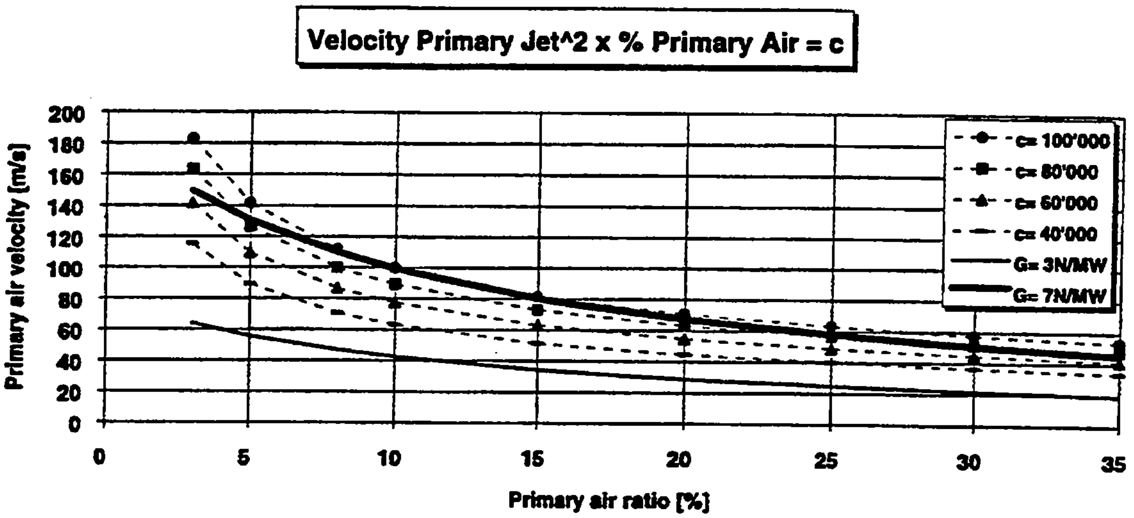
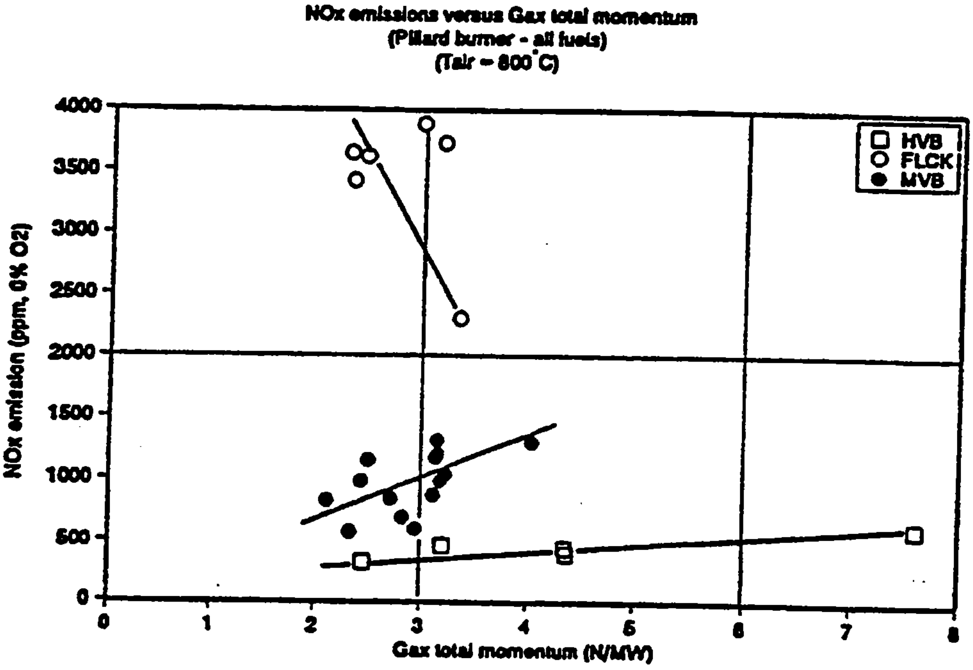


Figure 14: **Influence of Total Axial Momentum on NOx for a Pillard Multi Channel Burner**



5.3.5.3 Tangential Momentum and Swirl Level on the Swirling Channel

The second parameter affecting the entrainment into the flame is the tangential momentum. In general higher tangential momentum results in more rapid heat release in the near burner zone and higher NOx emission levels.

5.3.5.4 Swirling and Axial Air Amount, Distribution and Velocity

One of the main parameters affecting the tangential momentum is the swirling air and axial air distribution and injection velocities. In combination the product massflow (kg/s) times velocity (m/s) forms the momenta (N) on the different channels. It can be noticed that both swirling air velocity and amount may have a different influence on the flame characteristics.

5.3.6 Evaluation of Characteristical Burner Data (CETIC Working Group)

During the meetings 1995/96 of the CETIC working group focusing on kiln burners a database containing a total of 42 kiln burners could be established. In particular it was one of the main topics to investigate the NOx behavior of the individual kiln burner systems.

Due to the heterogeneity of the kiln and cooler systems as well as the different fuels used, direct comparison and correlation of the existing data is limited. However certain operational guidelines and tendencies can be given.

5.3.6.1 Burner Settings / Operational Figures / Correlations

Mono Channel Burner

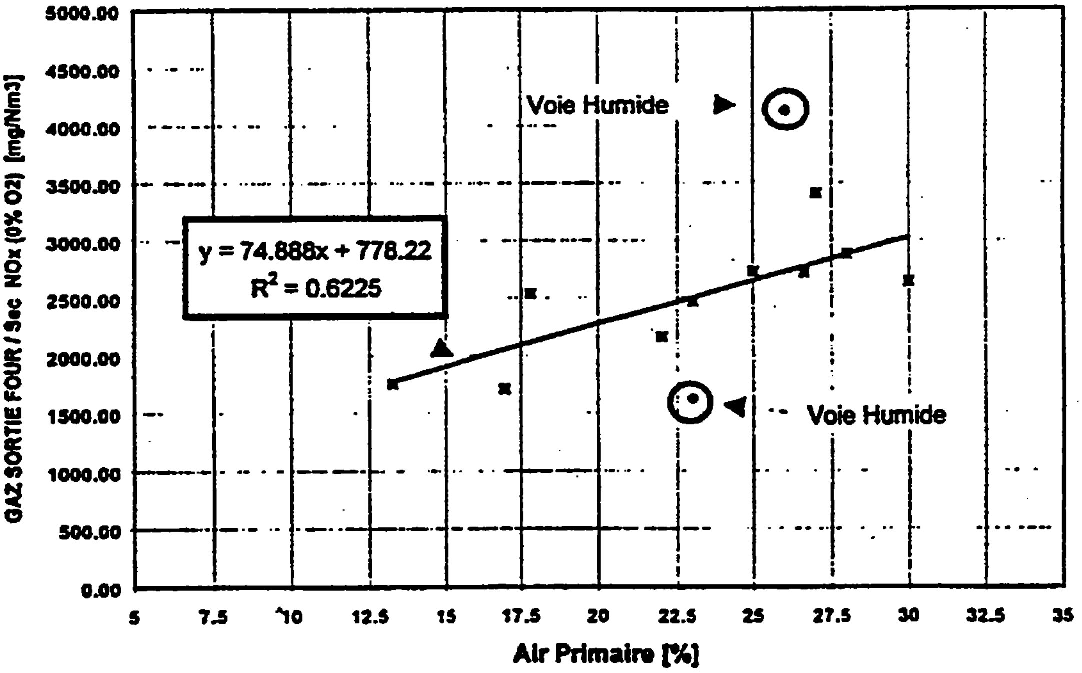
The evaluation of a total of 12 industrial mono channel burners is showing the following application range:

Primary air ratio	% Amin.	13 - 30	[%]
Injection velocity	v	60 -100	[m/s]
Specific axial momentum	G_{ax}	4.5 - 8.5	[N/MW]
Percentage of petcoke burned	% Petcoke	0 - 100	[%]
Kiln inlet NOx at 0% O_2	NO_x @ 0% O_2	1750 - 3400	[mg/Nm^3]
Secondary air temperature	T_{sec}	550 - 1000	[°C]

Primary air ratio

High primary air ratios must be avoided. This has negative effects both on kiln heat consumption and on NOx emissions. The CETIC data correlation for mono channel burners, primary air ratio vs NOx emission, clearly showed a rise in NOx at higher primary air ratios.

Figure 15:



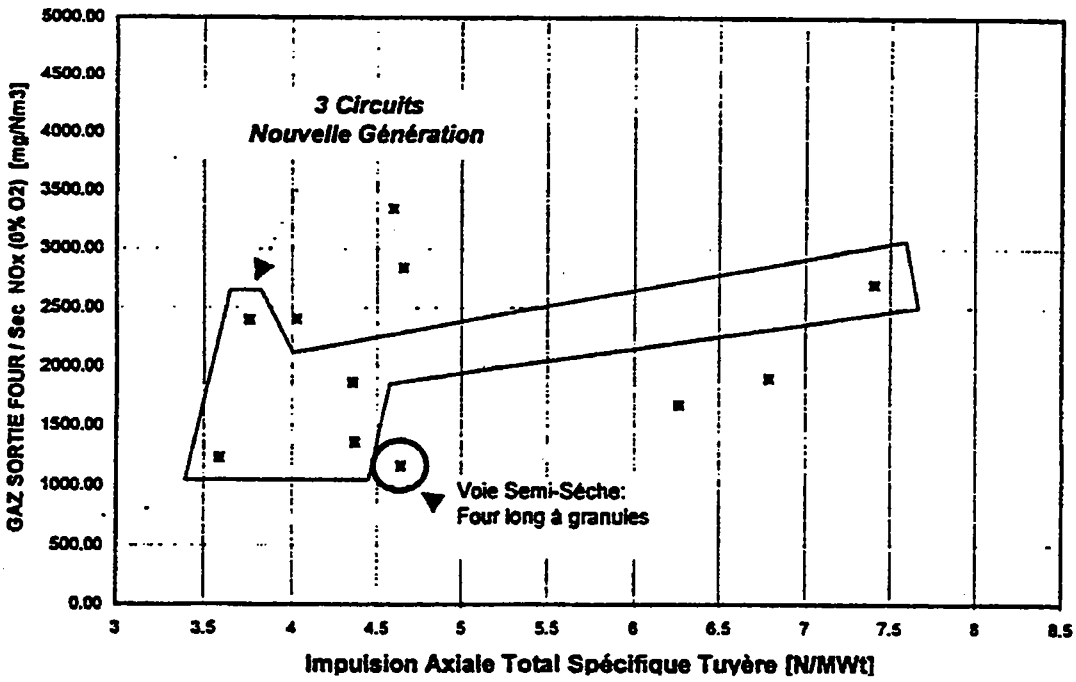
Multi Channel Burner

Primary air ratio	% Amin.	6 - 19	[%]
Percentage axial air		1.9 - 7.2	[%]
Percentage radial air		1.25 - 9.8	[%]
Percentage transport air		2.3 - 5.3	[%]
Injection velocity axial air	v_{ax}	90 - 300	[m/s]
Injection velocity radial air	v_{rad}	60 - 130	[m/s]
Injection velocity transport air	v_{tr}	14 - 38	[m/s]
Specific axial momentum	G_{ax}	3.6 - 7.4	[N/MW]
Percentage of petcoke burned	% Petcoke	0 - 100	[%]
Kiln inlet NOx at 0% O_2	NO_x @ 0% O_2	1160 - 3350	[mg/Nm³]
Secondary air temperature	T_{sec}	800 - 1010	[°C]

Specific axial momentum

For multi channel burners the impact of the specific axial momentum on NO_x emissions could be confirmed (see following graph). The specific axial momentum G_{ax} [N/MW] is in the range of 3.6N/MW up to 7.4 N/MW - very good coincidence with the 3 - 7 N/MW indicated in the Cemflame 1 research report.

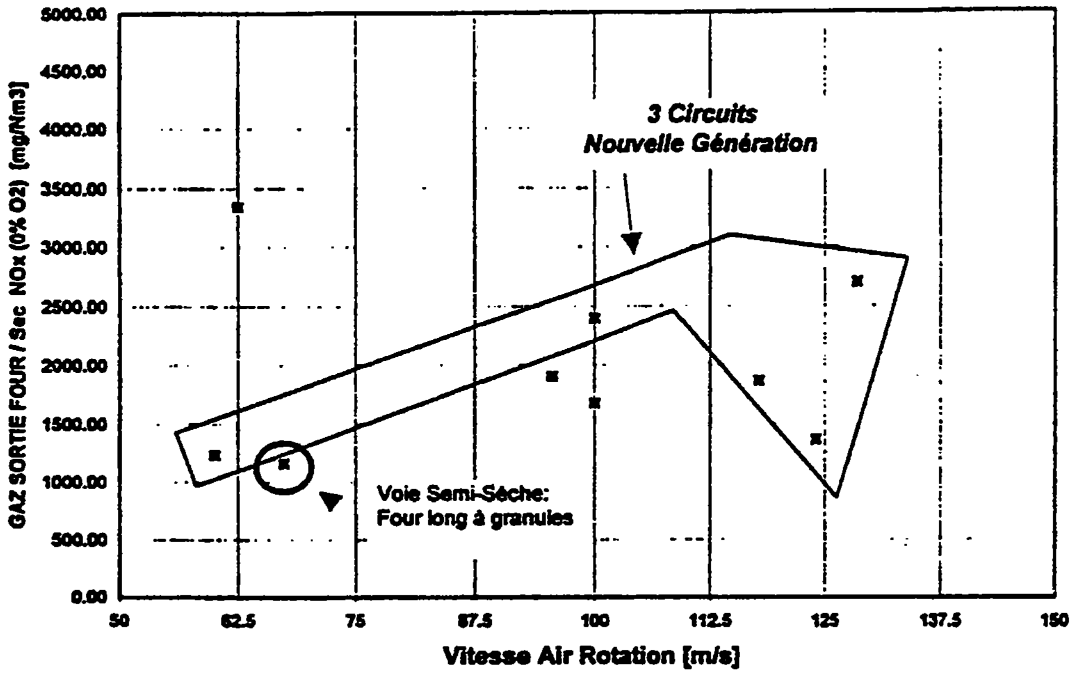
Figure 16:



Radial air velocity

From the CETIC test results further can be observed, that with increased radial velocity NOx emissions tend to be higher. This can be explained with a more rapid heat release in the near burner zone due to a higher tangential momentum.

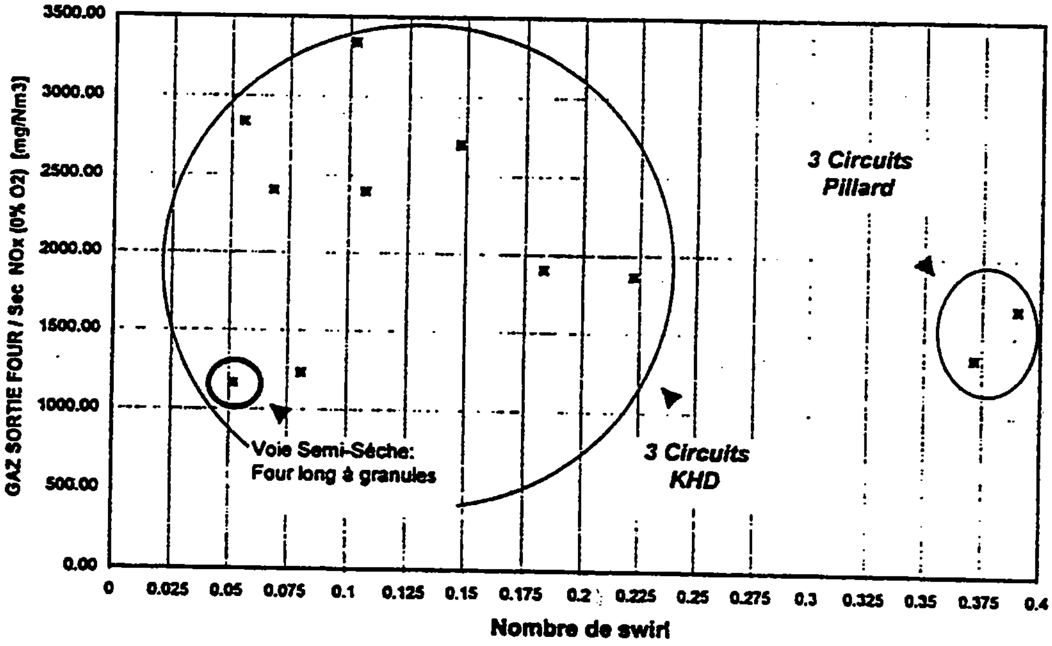
Figure 17:



Swirl number

The CETIC attempt to correlate the swirl number with respective NOx emissions was not very successful. It is however noticeable, that the Pillard burners showed by far the highest swirl numbers.

Figure 18:



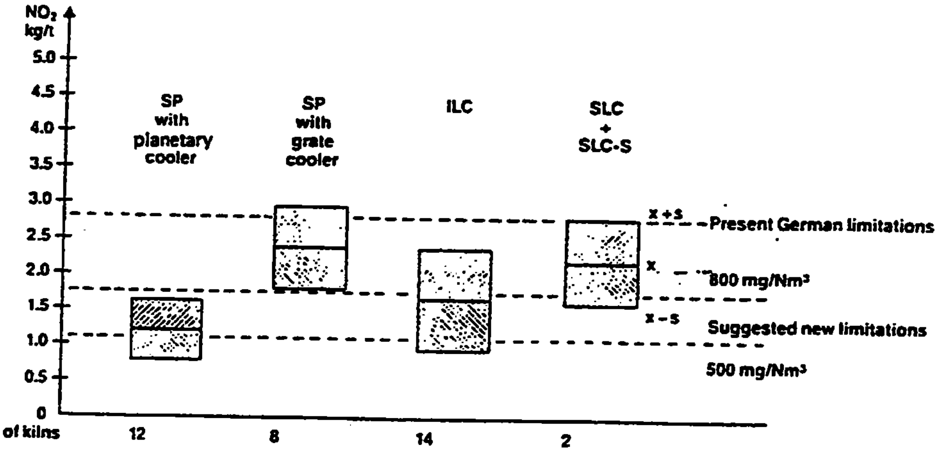
5.3.6.2 Influence of Cooler System on NOx Emissions

The following graph from reference [14] is showing the important effect of the cooler system on NOx emissions.

The grate cooler generating a hot, comparatively clean secondary air has considerable higher NOx output than the planetary cooler with its dusty secondary air, supposing identical kiln system for both cooler systems.

Mean value and standard deviation of measured NOx emission from different types of kiln systems.

Figure 19:



Number of kilns	12	8	14	2
Average	1.20	2.37	1.66	2.22
Standard deviation	0.42	0.58	0.72	0.58

6. NO EMISSION REDUCTION POSSIBILITIES

To reduce the NO emission from a pyroprocessing system to a certain controlled level, three basically different methods are available:

- Maintain the existing process while reducing the nitrogen input into the system
- Modify the existing process (primary reduction measures)
- Maintain the existing process while adding a separate gas cleaning unit for the exhaust gas (secondary reduction measures)

6.1 Reduction of Nitrogen Input

It is not economical to reduce the nitrogen content in the combustion air. However, a reduction of fuel-N for the secondary or precalciner firing may be feasible under certain conditions.

6.2 Primary Measures

Primary measures are all actions which directly influence the burning process.

6.2.1 Kiln / Clinker Cooler

- The criteria for a low NO generation are:
- constant fuel and kiln charge flow (short and long term)
- constant fuel and kiln charge composition
- constant secondary air flow and temperature
- lower burning zone temperature i.e. higher free lime
- lower LSF i.e. lower combinability (sintering) temperature
- lower flame temperature by
  - dust injection
  - water injection
  - alternative fuels with high H_2O content
- flame front closer to the burner by
  - bluff body
  - higher volatile coal
- low excess air factor
- lower primary air i.e. indirect firing, low primary air burner
- optimum distribution of primary air i.e. customized multi channel burner
- short retention time of the exhaust gas in the flame and the kiln
- minimum temperature fluctuations in kiln and cooler

To satisfy the first point an accurate dosing system and fuel transport is required.

A constant fuel quality is difficult to achieve, especially if waste fuel is used. Therefore, additional effort is needed for homogenization, preparation and analysis of the fuels.

The amount of heat from the secondary air depends mainly on operating characteristics of the clinker cooler. The new grate plates (for the recuperating zone) developed during the last years, help to stabilize the cooler operation and the heat input into the kiln.

A constant kiln and cooler operation is a prerequisite for optimizing of the excess air factor without reducing conditions for the clinker burning. The excess air factor (l) for the main burner is always above 1.

NOx reduction measures at the burner should achieve a reduction of temperature peaks and low oxygen content in the flame. Temperature peaks can occur if at a multi channel burner air volume and exit angle of swirl and axial air are not adjusted properly and if the fuel flow is fluctuating. Therefore, the burner should have a wide

adjusting range. The optimum operating point has to be determined with systematic long time tests.

The most important factor for NO generation is the ignition distance (= distance between burner exit and ignition of the fuel). An extension of the distance is increasing the NO generation. The reason for this behavior is the degree of total air (O_2) mixed with the fuel which is higher for longer distances.

To reduce the total air mixed into the fuel, primary air flow and total burner momentum should be kept as low as possible.

The operation of LINKman is at most effective when burners are operated near their optimum momentum and can in fact lead to lower NO levels, due to lower burning temperatures via better control.

To reduce the temperature of the secondary air the tertiary air should be extracted from the cooler at the kiln hood.

To shorten the retention time of the exhaust gas in the hot kiln, the gas speed in the kiln should be as high as possible. The limits for the gas speed are dust circulations and mechanical stress for the refractory materials. The upper limit for the specific fuel heat input is 7 MW / m^2 which is about equal to a specific exhaust gas flow of 2.5 kg/m^2s.

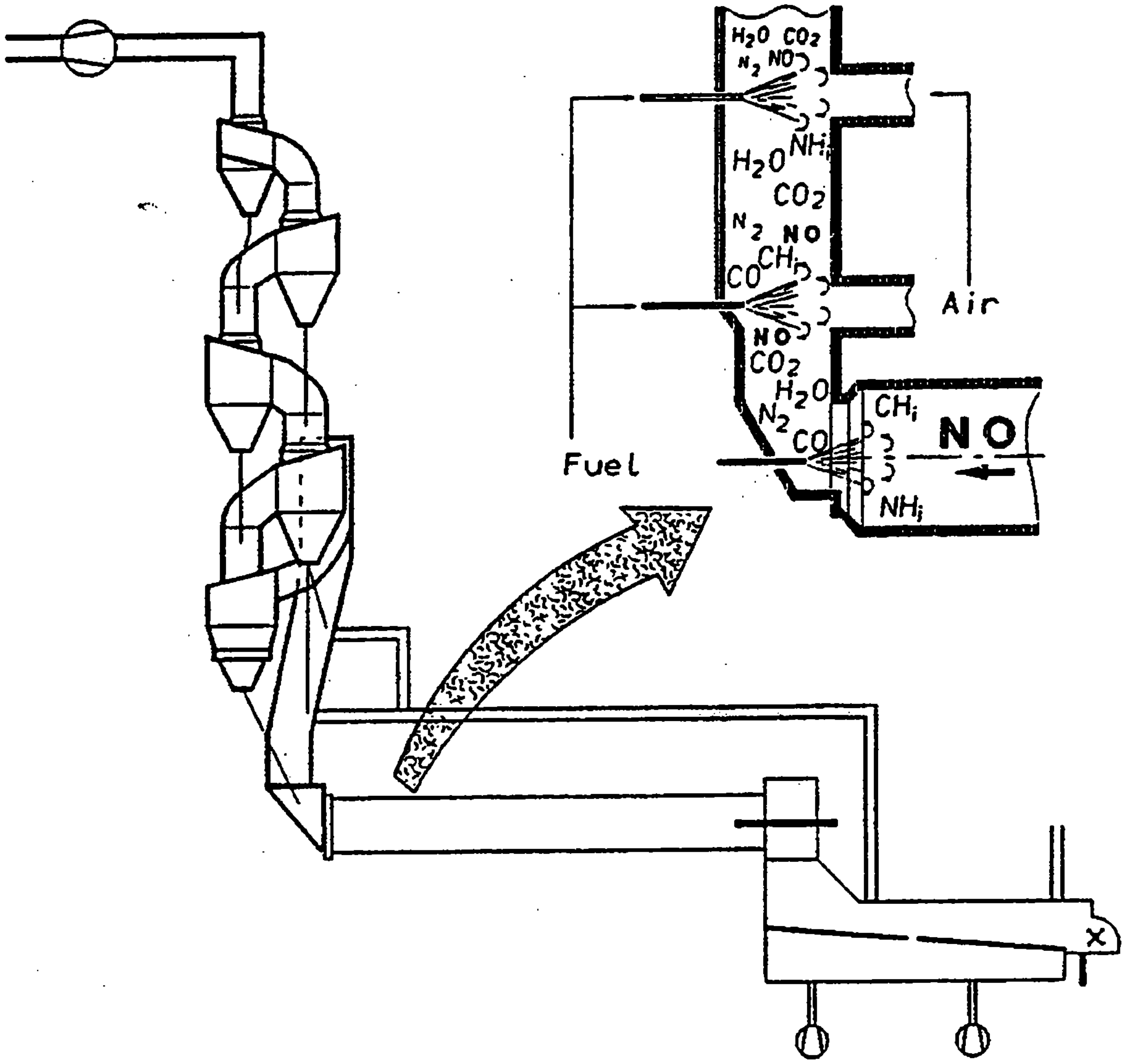
The minimum NO concentration with an optimized low NOx burner which can be achieved today is about 800 - 1000 mg NO_2 / Nm^3.

6.2.2 Secondary Firing / Multi-Stage Combustion

Mainly fuel-N is contributing to the NO formation (fuel-NO). It is possible to design the secondary firing in such a way that only little NO is produced and that a portion of the NO from the kiln is reduced. This can be achieved with a multi stage combustion [8].

Multi-stage combustion has turned out to be a suitable method for conventional and also for highly sophisticated clinker burning processes. In the first combustion stage which extends over the sintering zone and the transition zone in the rotary kiln, combustion takes place in an oxidizing atmosphere (excess air coefficient > 1) to ensure good clinker quality. The nitrogen oxides which are inevitable formed in this high temperature zone are partially decomposed in a second combustion stage which has, at least locally, a reducing atmosphere (excess air coefficient < 1).

Figure 20: NOx reduction by Multi Stage Combustion



By introducing fuel through a burner in the kiln inlet zone a reducing environment is set up in this second combustion stage. The resulting intermediate products from the consecutive reactions of combustion act as reducing agents for NO created in the sintering zone and at the same time prevent the formation of more NO. This reaction pattern is shown diagramatically in Fig. 12 for a precalciner plant of the PREPOL-AS type. Multi-stage combustion is logical in precalciner plants in order to avoid renewed formation of nitrogen oxides in the calciner from nitrogen in the fuel.

A part of the precalcining fuel is introduced in the kiln inlet to form a reducing zone by arranging an air deficiency (< 1). The rest of the precalcining fuel is also supplied to the calciner, at least partially, in a reducing zone. This fuel burns here under sub- stoichiometric conditions (excess air coefficient < 1) and thus suppresses formation of NOx from the nitrogen in the fuel. In a fourth stage the unburned flue gas constitutients from the reducing zone are fully oxidized by supplying hot combustion air, whereby a turbulence generating gas flow in the calciner serves to enhance the burnout process.

6.2.3 Possible Negative Side Effects of Primary Measures

Kiln burner

Temperature reduction:

- reduction of production capacity
- higher power and heat consumption
- clinker quality

Oxygen (excess air, primary air) reduction:

- clinker quality
- additional CO formation
- additional SO_2 volatilization
- additional TOC emissions

Secondary combustion

Lower fuel-N concentration:

- higher fuel cost

Staged combustion:

- additional CO formation
- additional TOC emissions
- difficult to control

6.3 Secondary Measures

Secondary measures are exhaust gas treatments mainly SNCR (selective non-catalytic reduction) or SCR (selective catalytic reduction).

In some cases combustion of coarse fuel (tires) in the kiln inlet is also considered as a secondary measure. Because of the reducing condition of the waste fuel combustion, NO is reduced to N_2. This reaction is called NSNCR (non-selective non-catalytic reduction).

The most efficient secondary measure which is already in operation in several kilns is the SNCR with NH_3.

6.3.1 The Selective Non-Catalytic Reduction

From tests in cement works it is known that ammonia, when injected into certain temperature zones of the cement kiln is able to reduce a large proportion of the nitrogen monoxide.

In this chapter the NH_3-injection is described.

The Reaction Mechanism

The desired process of reducing nitrogen monoxide (NO) by ammonia (NH_3) is initiated by dissociation of the injected ammonia. At room temperature ammonia is stable, but at roughly 600 to 800°C a marked thermal decomposition is initiated by the reaction:

$$NH^{\bullet}_2 + O H^{\bullet} \rightarrow NH_2 + H_2O \qquad (13)$$

As the reaction proceeds, the NH_2 radical is responsible for the reaction of nitrogen monoxide (NO).

$$N H^{\bullet}_2 + NO \rightarrow N_2 + H_2O \qquad (14)$$

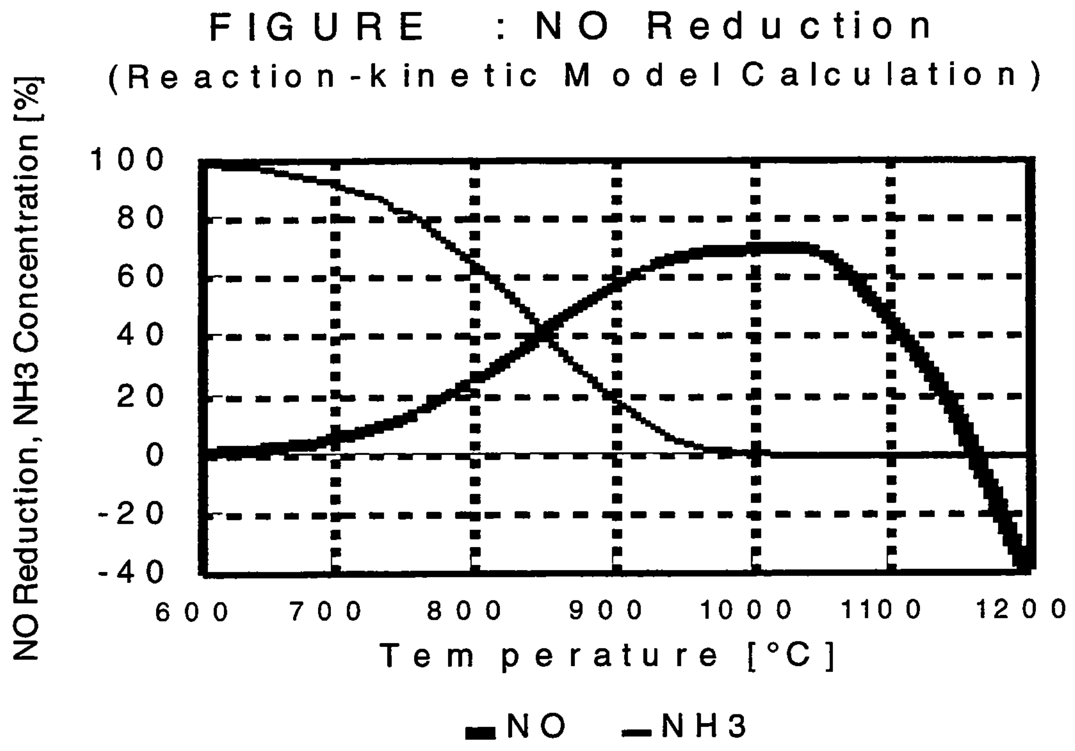
The Influencing Factors

Temperature Window

Reduction of nitrogen monoxide (NO), defined as the decrease in NO relative to the original NO, is a function of the temperature where the ammonia is injected and the reaction is made. As Fig. 13 shows, a high NO reduction is only achieved in a narrow temperature band. This is generally referred to as the "temperature window". In a normal flue gas from a cement kiln the maximum reduction of nitrogen monoxide (NO) is attained at about 950°C.

In a cement kiln at the most the temperature zone between 900 and 1100°C is technically "accessible". This means that the temperature zone is located in the preheater and this is where the ammonia can be injected. For this injection only the "lower" (left-hand) part of the NO reduction curve in Fig. 13 can be used.

Figure 21: NO-Reduction (Reaction-kinetic Model Calculation)



Dwell Time

The formation of the NH_2 radical from the ammonia (equation [?]) is dependent on the time. When ammonia is injected in to the cement process, this dwell time is fixed by the process. In any case the injection points in a cement kiln must be chosen that this dwell time is as long as possible.

Ammonia Slip

The proportion of injected ammonia that does not decompose to NH_2 radicals is called the NH_3 slip. This proportion leaves the reaction zone and travels with the flue gas to colder regions, during which a small proportion can decompose to NH_2 radicals. The greater part of the slip, though, will remain stable as ammonia and, following various adsorption processes in the preheater, the cooling tower, the raw mill, or the electrostatic precipitator, will finally be emitted through the chimney as gaseous ammonia or adsorbed by aerosols.

Because only the "lower" (left-hand) part of the NO reduction curve in Fig. 2 can be used, in any case a noticeable NH_3 slip in this temperature zone occurs.

Injection Rate

The nitrogen monoxide reduction rate rises with increased NH_3 injection rate, but work tests have shown that a greater injection rate will produce a greater ammonia slip. In cement kilns ammonia should only be injected up to a mol ratio of 1.5 at the most, or in extreme cases 2.

$[NH_3]/[NO_0]< 1.5$ $\qquad$ $NO_0 \rightarrow$ N= without reduction

Form of Injected Ammonia

Pure Ammonia

Ammonia is already fluid at low pressures (15°, 7.28 bar). This substance can therefore be stored in a pressurized tank and pumped as a liquid. The entire ammonia system must be dimensioned for a pressure of 20 to 30 bar, which is certainly not optimal and can cause problems with the permission of such a tank in a cement plant.

Ammonia Water

For an ammonia injection in a cement kiln ammonia water (NH_4OH solution) should be used. In this solution the greater part of the ammonia is present in hydrated form as NH_3H_2O and only a very small proportion has dissociated to ammonium (NH_4^+) and hydroxide ions (OH^-). When heated rapidly from ambient temperature to the reaction temperature, the solution decomposes into water (H_2O) and ammonia (NH_3). Thus ammonia water has the same effect as pure ammonia but the problems with transport, storage, handling, etc. are much less.

Alternatives to Ammonia

It is postulated and proved by works tests that the reduction of the nitrogen monoxide (NO) is effected via the NH_2 radical. This means that all substances capable of supplying an NH_2 radical may be used for reduction of NO.

A component of this kind is, for instance, urea $CO(NH_2)_2$. This substance decomposes approximately in the same temperature zone, thereby producing NH_2 radicals but unfortunately also a $CONH_2$-radicals. That means urea decomposes according to reaction [4] and not according to reaction.

$$CO\,(NH_2)_2 \rightarrow CO + 2\,(N\,H^{\bullet}_2) \qquad (15)$$

$$CO\,(NH_2)_2 \rightarrow CO + N\,H^{\bullet}_2 + NCON\,H^{\bullet}_2 \qquad (16)$$

About the behavior of the $CONH_2$-radical up to now nothing is know, but it is possible that cyanide compounds are produced in the kiln system.

6.4 Effectiveness of NOx Reduction Measures [9]

Figure 22: Comparison of NOx Control Technologies for Cement Kilns

Control Technology	Technical Feasibility	Potential NOx Reduction	Relative Cost	Effect on Clinker Quality	Effect on Other Emissions
CM	Medium (both kiln types)	15 - 30%	Low	May be adverse	CO, THC, SO_2 may increase
LNB	High (both kiln types)	15 - 30%	Low	• Improved • May vary with installation	• CO, SO_2 may increase • may vary with installation
SAC	High (precalciner kilns)	20 - 50%	Low	None	CO, THC may increase
SNCR	Medium (precalciner kilns)	40 - 70%	Medium	None	Potential for NH_3, PM_{10} emissions
NSNCR	Medium (all kilns)	20 - 30%	Low	None	CO, THC, SO_2 may increase

CM = Combustion Modifications
LNB = Low NOx Burner
SAC = Staged Air Combustion
SNCR = Selective Non-Catalytic Reduction
NSNCR = Non-Selective Non-Catalytic Reduction

7. EXAMPLES OF NOX EMISSION REDUCTION

A collection of short descriptions of plants and their measures against NOx emissions is enclosed. Everybody is welcome to contribute to this collection.

NO_x emission reduction

Plant:	Siggenthal (SG)
Capacity:	2000 t/d (design), 1900 t/d (standard)
Fuel type	Fuel oil, dried sewage sludge, complete tires [1]
Plant description:	Kiln with 4-stage preheater
Supplier/equipment:	Polysius kiln and preheater (Dopol), Fuller grate cooler
Initial NO_X emission problem:	Very high NO_X emissions of up to 2800 mg/Nm^3_{dry} (in direct operation) were reported in 1987. (LRV-limit = 1500 mg/Nm^3_{dry}, since 1991 LRV-limit = 800 mg/Nm^3_{dry}) [LRV = Swiss clean air act]
Solutions investigated:	In 1988 trials to reduce the NO_X emissions by injection of Ammonia-water in the raiser duct were carried out. Reductions of up to 46% were reached. The problem of this reduction method was the high NH_3 emission due to the NH_3 in the raw meal, which was already higher than the emission limit. So any small additional NH_3 amount would not be acceptable. [3] Using a Pyrojet low-NO_X burner, the emissions in 1990 were around 1500 mg/Nm^3_{dry}. [2] SG had a project to burn sewage sludge containing Hg and at the same time the NO_X and SO_2 emissions where much too high. To solve these problems, a 3-stage waste gas cleaning system was foreseen. In 1990 the system was successfully tested in a pilot plant with an Ammonia-water injection into the riser duct as well as an active coke filter. Using this SNCR, NO_X could be reduced to N_2 and H_2O with ammonia injection. In these trials a reduction of the NO_X emissions by more than 60% and hence below 800 mg/Nm^3_{dry} was reached.
Solution realised:	Based on the experiences of the pilot plant, a denitrification system, based on SNCR was built. This system is followed by the kiln EP and a POLVITEC (Polysius Environmental Technology) active coke scrubber, which is mainly filtering out SO_2 and Mercury but also other pollutants like heavy metals, eventually occurring NH_3 from the denitrification and organics. The whole system was successfully commissioned in 1994. Investment cost: 30'000'000 CHF Operating cost: 3.3 CHF/t cli
Emissions reached:	< 800 mg/Nm^3_{dry} [4]
Literature:	[1] ATR, Annual Technical Report 1994,"Holderbank" [2] Stenger, Dr. R., Informationsveranstaltung der PCW Siggenthal zum Thema Klärschlamm-Verbrennung / Abgas -reinigung, HMB Bericht MA 92/93/D, VA-Dok: SG, Reg. 2 [3] Waltisberg, J., Die Reduktion der NO_X-Emission durch Eindüsung von Ammoniak in den Vorwärmer, HMB Bericht MA 88/10686/D, VA-Dok: SG, Reg. 2 [4] Effektive Emissionsminderung bei Einsatz von Sekundärbrennstoffen im Zementdrehofen von "HCB Siggenthal, Dr. D. Rose, Dr. L. Brentrup, Krupp Polysius

Figure 22: Integration of a POLVITEC-Filter in a cement plant

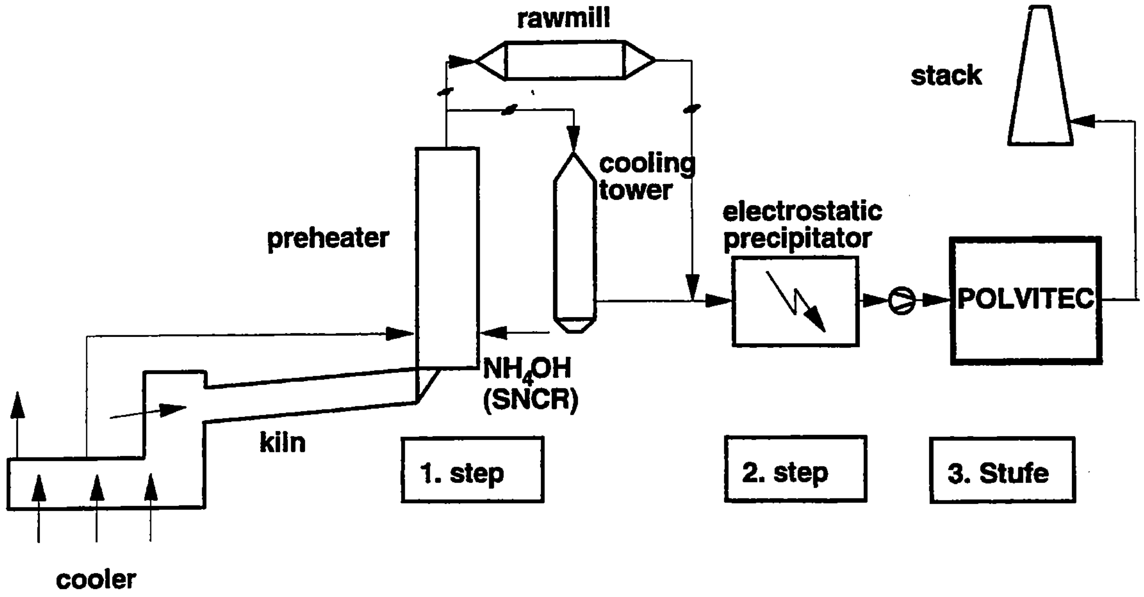
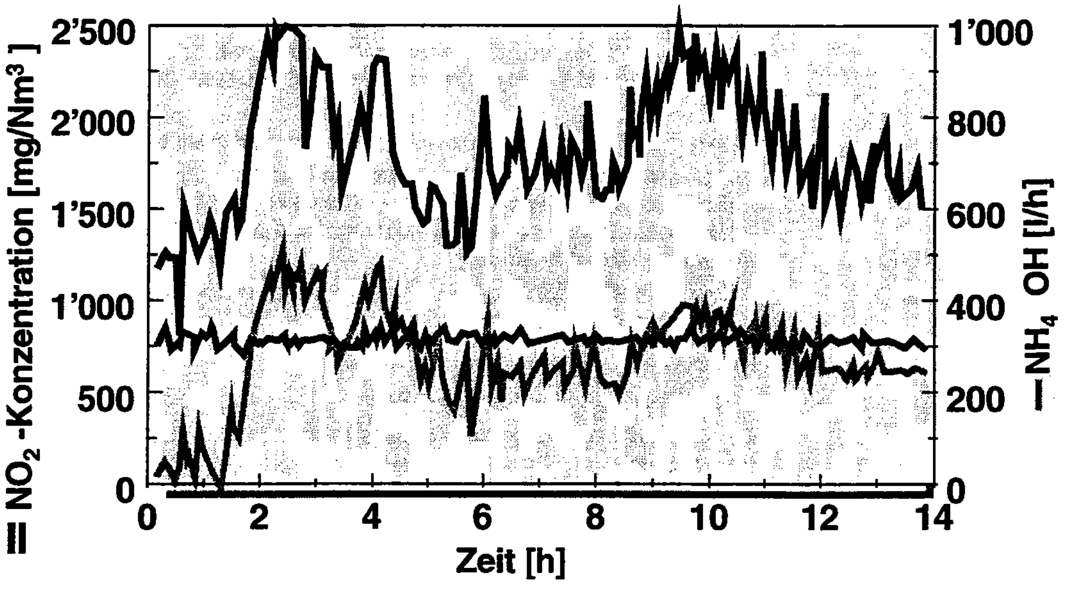


Figure. 23: Effect of SNCR of NOx at the Siggenthal plant. The NOx emission is controlled to below 800 mg/Nm$^3_{dry}$



NO_x emission reduction

Plant:	Untervaz (UV)
Capacity:	1900 t/d (standard)
Fuel type:	Coal, fuel oil; alternative fuels as dried sewage sludge, waste oil, distillation residue, plastics [1]
Plant description:	Kiln with 4-stage-suspension preheater and planetary cooler (kiln III)
Supplier/equipment:	KHD kiln, preheater and cooler
Initial NO_x emission problem:	In January 1985 NO_x emissions of 770 mg/Nm$^3_{dry}$ were measured. After changing the original Pillard burner to a new Pyrojet burner, and additional changings on the lining (dam ring), in June 1985 a NO_x emission 360 mg/Nm$^3_{dry}$ was reported. [2]. In this time, only coal was used as fuel. Later, using a mixture of coal and oil, the flame was not any more as stable as before, and the NO_x emission became higher. During measurements in 1989 for the office of environment the following NO_x emissions were measured: [3] 880 mg/Nm$^3_{dry}$ in compound operation 950 mg/Nm$^3_{dry}$ in direct operation (LRV-limit = 1500 mg/Nm$^3_{dry}$, since 1991 LRV-limit = 800 mg/Nm$^3_{dry}$) [LRV = Swiss clean air act]
Solutions investigated:	In 1990 the reduction of NO by injection of Ammonia-water or urea was tested at different locations in the preheater tower. By injection of Ammonia-water in the raiser duct on stage 4 of the heatexchanger, a NO reduction of up to 42 % of the initial 840 mg/Nm$^3_{dry}$ could be achieved [4]. After these short trials, a further test to add Ammonia-water to the preheater has been carried out in 1991. The achieved reduction was about 50 %, depending also on the ratio NH_3/NO, i.e. approx. to 400 - 500 mg/Nm$^3_{dry}$. Compared to the addition of urea, the achievable reduction with Ammonia-water was twice as high.[5] The influence of water in the waste oil was investigated in 1992. Without negatively influencing the temperature of the sintering zone, a maximum of 5.7 g H_2O/kg clinker could be injected, which resulted in a NO-reduction of 20 - 25%. [6] In 1993 a test to reduce NO selective and non-catalytic with pure hydrogen was carried out at temperatures between 600 and 1600 °C, without success. [7]
Solution realised:	Actually the NO_x emissions are kept at a low level due to the low-NO_x-burner and the water contained in the waste oil and in distillation residues. Additionally the Linkman control as well as a rather high CO concentration and the dusty atmosphere in the burning zone due to the planetary cooler contribute to a low NO-level.
Emissions reached:	In spring 1993 the following NO emissions of the kiln (calculated as NO_2) have been measured: [8] 540 mg/Nm$^3_{dry}$ in compound operation 600 mg/Nm$^3_{dry}$ in direct operation The averaged values of 1994, measured after the heatexchanger, were in the same range.
Further Optimisation:	Is actually not necessary. If ever it would be necessary, the possibility of adding Ammonia-water to the preheater could be envisaged again.

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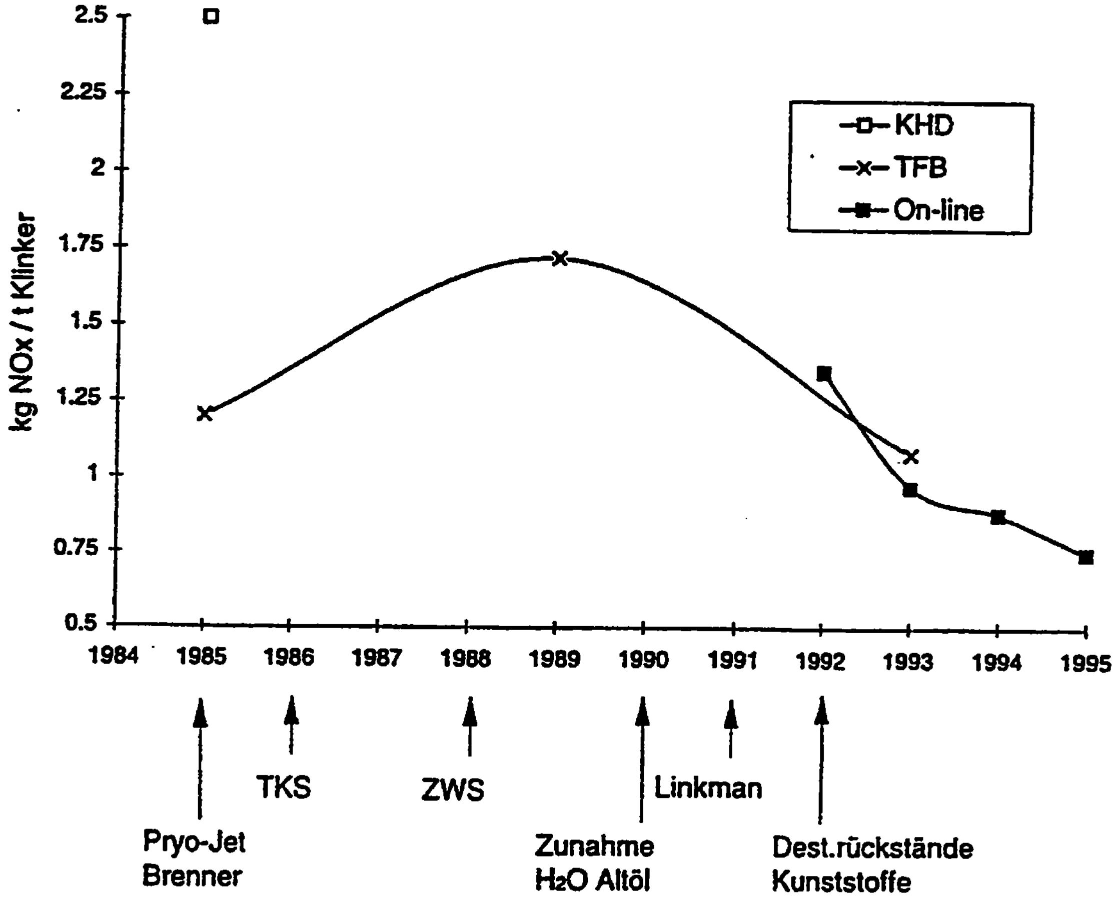
Figure 24: NOx-Emissions BCU (kiln #1)



NO$_x$ emission reduction

Plant:	Rekingen (RK)
Capacity:	2'200 mtpd (design), 2130 mtpd (standard)
Fuel type:	Coal, fuel oil, waste timber
Plant description:	4-stage-suspension preheater kiln
Supplier/equipment:	Polysius kiln and preheater
Initial NO$_x$ emission problem:	NO$_x$ emissions used to be very high in the past, and have not frequently been measured. In about 1984, the systematic observations and measurements of these emissions was started. As an example, in 1985 NO$_x$ emissions of about 1800 mg/Nm^3 (based on 3 % O$_2$) were measured. [1] (LRV-limit = 1500 mg/Nm$^3_{dry}$, since 1991 LRV-limit = 800 mg/Nm$^3_{dry}$) [LRV = Swiss clean air act]
Solutions investigated:	Initially the influences of different parameters on the existing plant have been investigated, as for example the temperature of the burning zone, the amount of primary- and secondary air, coal as well as raw meal [1]. In 1990 the actual NO$_x$ emissions were reported as 1'200 mg/Nm$^3_{dry}$ in direct operation and 950 mg/Nm$^3_{dry}$ in compound operation. These values have been below the actual valid LRV-limit of 1'500 mg/Nm$^3_{dry}$. Due to a regulation of the state of Aargau, a further reduction of the total NO$_x$-emissions from 1200 t/year to about 300 t/y was required. It was expected to reach this reduction by installing a new Pyrojet burner (awaited REDUCTION OF ABOUT 30 - 40 %) and a additional denitrification based on SNCR (awaited reduction of about 60%) [2]. Through the installation of a new Pyrojet low-NO$_x$-burner in 1990, the NO$_x$-emissions were reduced to around 800 mg/Nm$^3_{dry}$. The denitrification has then first been investigated in trials, by adding liquid ammonia or urea to the preheater. The best results in the trials have been achieved, adding liquid ammonia into the raiser duct between preheater stage 3 and 4. Depending on the NH$_3$/NO ratio NO$_x$-reductions of up to around 50% could be detected [3] Due to unstable burning characteristics (design problem) which lead to higher NO$_x$ emissions, the Pyrojet low-NO$_x$ burner was exchanged in 1993 again to a Pillard 3 -channel burner (same type as earlier).[4] With this burner NO$_x$ emissions of 720 mg/Nm$^3_{dry}$ could be reached.
Solution realised:	In 1994 a 4-channel Rotaflam burner was installed, mainly to be able to use waste timber as alternative fuel.
Emissions reached:	With the Rotaflam burner the NO$_x$ emissions were reduced by 10 20 % to an average value of 650 mg/Nm$^3_{dry}$.

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NO_x emission reduction

Plant:	Hardegsen (HD)
Capacity:	1'086 mtpd (standard)
Fuel type:	Coal (>98%), fuel oil, natural gas, landfill gas [1]
Plant description:	4-stage-suspension preheater kiln with grate cooler
Supplier/equipment:	MIAG kiln and Fuller cooler
Initial NO_x emission problem:	Until 1989 the NO_x emissions using a Pillard VR-K3 three chanel burner were in the range of 1300 mg/Nm^3_{dry} (based on 10 % O_2) [2,3]. (TA Luft-limit = 1800 mg/Nm^3_{dry}, since 1991 the limit is 800 mg/Nm^3_{dry} for old plants and 500 mg/Nm^3_{dry} for new plants.)
Solutions investigated:	Different low-NO_x burners were investigated. Finally the decision for a Pillard Rotaflam burner was influenced by the lower investment costs, the use of the existing pipe lines and the entire burner suspension system and the fact, that one of the existing fans could be reused.
Solution realised:	In 1990 a Rotaflam low-NO_x burner was installed and is operated since then with good experience.
Emissions reached:	The NOx emissions could be reduced by about 22% under comparable conditions to 1004 mg/Nm^3_{dry} in the acceptance tests.

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